

# Chiral one- to three-dimensional uranyl–organic assemblies from (1*R*,3*S*)-(+)-camphoric acid†

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Four complexes were obtained from reaction of uranyl nitrate with (1*R*,3*S*)-(+)-camphoric acid under solvo-/hydrothermal conditions with either acetonitrile or *N*-methyl-2-pyrrolidone (NMP) as the organic component. All complexes crystallize in chiral space groups and are enantiopure species. Complexes [(UO<sub>2</sub>)<sub>4</sub>(L)<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O (**1**) and [(UO<sub>2</sub>)<sub>6</sub>K<sub>8</sub>(L)<sub>12</sub>(H<sub>2</sub>O)<sub>12</sub>]·H<sub>2</sub>O (**2**) were obtained in water–acetonitrile in the presence of LiOH or KOH in excess beyond or equal to that simply required to neutralize the acid, respectively. Whereas **1** is a 1D coordination polymer including hydroxide ions resulting from hydrolysis of the uranyl aqua-ion, **2** contains octanuclear uranyl camphorate cages analogous, but for their crystallographic symmetry, to those previously published; these cages are assembled into a 3D framework by bridging potassium ions. The two complexes obtained in water–NMP, [UO<sub>2</sub>(L)(NMP)] (**3**) and [(UO<sub>2</sub>)<sub>2</sub>Cu(L)<sub>3</sub>(NMP)<sub>2</sub>] (**4**), are devoid both of water molecules and any solvent-derived anions, and they crystallize as 2D assemblies. The sheets in **4**, with a thickness of ~14 Å, display a central layer of copper(II) ions surrounded by two layers of uranyl ions. These and previous results suggest that solvo-/hydrothermal conditions using NMP provide a new means of avoiding the formation of uranyl-containing oligomeric or 1D polymeric hydrolysis products which are frequent and often unpredictable outcomes in the synthesis of uranyl–organic assemblies under aqueous conditions, especially in the presence of cosolvents which in themselves are susceptible to hydrolysis. The emission spectrum of compound **3** under excitation at 350 nm displays the usual vibronic fine structure in the ~460–600 nm range, while uranyl luminescence is quenched by Cu(II) cations in complex **4**.

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## Introduction

Of the huge number of metal–organic polymeric assemblies and frameworks which have been reported in the past years, those which are homochiral represent a subset of interest for various specific applications such as heterogeneous asymmetric catalysis or enantioselective separation.<sup>1</sup> Although such species can be assembled from achiral components through self-resolution or chiral induction,<sup>1e,2</sup> the most straightforward synthetic pathway uses enantiopure chiral ligands. Among these, the readily available (1*R*,3*S*)-(+)-camphoric acid (H<sub>2</sub>L) is particularly appealing since it possesses two carboxylic acid groups located in a suitable geometry to act as a bent, divergent linker between two metal cations, and it is not subject to racemization, even under hydrothermal conditions. Following the first report in 2003, nearly 200 crystallographically characterized camphorate complexes are presently found in the Cambridge Structural Database (CSD, version 5.34),<sup>3</sup> the majority

(about 150) of which contain d-block metal ions.<sup>4</sup> In the case of f-element cations, 29 camphorate complexes are known to have metals of the 4f lanthanide series,<sup>5</sup> but only four complexes with a 5f actinide cation, all involving the most common uranyl ion, have been described.<sup>6</sup> The first uranyl complexes, [UO<sub>2</sub>(L)(py)<sub>2</sub>]·py and [UO<sub>2</sub>(L)MeOH]·MeOH, were obtained under solvothermal (pyridine) or solvo-/hydrothermal (methanol–water) conditions, and they crystallized as zigzag chains or undulating sheets, respectively; in both cases, the organic solvent was present as an additional ligand.<sup>6a</sup> Moreover, the bent shape of the ditopic camphorate ligand makes it a suitable candidate for the design of cyclic uranyl-based species,<sup>7</sup> and this was achieved when the synthesis was performed under hydrothermal conditions in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) resulting in [(UO<sub>2</sub>)<sub>8</sub>(L<sub>12</sub>H<sub>8</sub>)]·12H<sub>2</sub>O, a chiral octanuclear cage complex.<sup>6b</sup> These cage complexes are assembled into a two-dimensional array through bridging by carboxylate-bound barium(II) cations in [Ba(H<sub>2</sub>O)<sub>8</sub>]<sub>2</sub>[(UO<sub>2</sub>)<sub>8</sub>Ba<sub>2</sub>(L<sub>12</sub>)(H<sub>2</sub>O)<sub>4</sub>]·8H<sub>2</sub>O, obtained in the presence of Ba(CH<sub>3</sub>COO)<sub>2</sub>.<sup>6b</sup> Considering the structural disparity between these uranyl camphorate complexes, it appeared worthwhile to investigate the influence of other experimental conditions on the outcome of the reaction. Four novel complexes were thereby obtained under solvo-/hydrothermal

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conditions with acetonitrile or *N*-methyl-2-pyrrolidone (NMP), which have previously been shown to be suitable for the synthesis of uranyl-organic coordination polymers or frameworks.<sup>7d,8,9</sup> The crystal structures of these complexes, two of which involve additional metal cations intended to induce aggregation of uranyl entities, are reported herein, as well as the luminescence properties of two of them.

## Experimental

### Synthesis

**Caution!** Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection.

UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (depleted uranium, R. P. Normapur, 99%) was purchased from Prolabo. (1*R*,3*S*)-(+)-Camphoric acid and Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O were from Aldrich. Elemental analyses were performed by MEDAC Ltd. at Chobham, UK.

[(UO<sub>2</sub>)<sub>4</sub>(L)<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O (1). (1*R*,3*S*)-(+)-Camphoric acid (20 mg, 0.10 mmol), UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (50 mg, 0.10 mmol), LiOH (10 mg, 0.42 mmol), acetonitrile (0.3 mL) and demineralized water (1.1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, producing light yellow crystals of complex 1 in low yield within one week. The yield could not be improved by more prolonged heating.

[(UO<sub>2</sub>)<sub>8</sub>K<sub>8</sub>(L)<sub>12</sub>(H<sub>2</sub>O)<sub>12</sub>]·H<sub>2</sub>O (2). (1*R*,3*S*)-(+)-Camphoric acid (20 mg, 0.10 mmol), UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (50 mg, 0.10 mmol), KOH (11 mg, 0.20 mmol), acetonitrile (0.3 mL) and demineralized water (1.0 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, producing light yellow crystals of complex 2 in low yield mixed with an amorphous powder within three weeks.

[UO<sub>2</sub>(L)(NMP)] (3). (1*R*,3*S*)-(+)-Camphoric acid (20 mg, 0.10 mmol), UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (50 mg, 0.10 mmol), *N*-methyl-2-pyrrolidone (0.3 mL) and demineralized water (0.9 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, producing light yellow crystals of complex 3 within one week (24 mg, 42% yield). Anal. calcd for C<sub>15</sub>H<sub>23</sub>NO<sub>7</sub>U: C, 31.75; H, 4.09; N, 2.47. Found: C, 31.80; H, 4.11; N, 2.50%.

[(UO<sub>2</sub>)<sub>2</sub>Cu(L)<sub>3</sub>(NMP)<sub>2</sub>] (4). (1*R*,3*S*)-(+)-Camphoric acid (20 mg, 0.10 mmol), UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (50 mg, 0.10 mmol), Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (23 mg, 0.10 mmol), *N*-methyl-2-pyrrolidone (0.3 mL) and demineralized water (1.1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, producing light green crystals (very thin platelets) of complex 4 within one week (26 mg, 56% yield based on camphoric acid). Anal. calcd for C<sub>40</sub>H<sub>60</sub>CuN<sub>2</sub>O<sub>18</sub>U<sub>2</sub>: C, 34.40; H, 4.33; N, 2.00. Found: C, 34.40; H, 4.24; N, 2.07%.

### Crystallography

The data were collected at 150(2) K using a Nonius Kappa-CCD area detector diffractometer<sup>10</sup> with graphite-monochromated

Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames then refined on all data. The data (combinations of  $\varphi$ - and  $\omega$ -scans with a minimum redundancy of 4 for 90% of the reflections) were processed using HKL2000.<sup>11</sup> Absorption effects were corrected empirically using the program SCALEPACK.<sup>11</sup> The structures were solved by direct methods using SHELXS-97, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on  $F^2$  using SHELXL-97.<sup>12</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on Fourier-difference maps (except in some cases indicated below), and the carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH<sub>3</sub>). All compounds crystallize in chiral space groups, and the absolute configuration determined from the refined Flack parameter<sup>13</sup> is in agreement with that of the camphorate enantiomer used, although the values deviate significantly from 0 by more than twice the standard uncertainty. The special details are as follows:

**Compound 1.** The structure, with two formula units in the asymmetric unit, is close to being centrosymmetric ( $P2_1/c$ ) and refinement in  $P2_1$  is quite unstable. As a consequence, many restraints on bond lengths and displacement parameters had to be applied. The hydrogen atoms bound to oxygen atoms were found on a Fourier-difference map only for the hydroxide groups and seven water molecules (of which four are coordinated and three are free) but not for the other water molecules.

**Compound 2.** For charge equilibrium and in order to retain acceptable displacement parameters, two out of the four K atoms were given occupancy parameters of 1/3. Many restraints on bond lengths and displacement parameters had to be applied. The hydrogen atoms bound to water oxygen atoms were not found nor introduced. Large voids in the lattice probably indicate the presence of other disordered water solvent molecules.

**Compound 3.** One NMP molecule is disordered over two positions sharing the oxygen and one carbon atom, which have been refined with occupancy parameters constrained to sum to unity. Restraints on some bond lengths, angles and displacement parameters have been applied, particularly for the atoms of the disordered part.

**Compound 4.** The two half-camphorate ligands in the asymmetric unit, both with the other half generated by a two-fold rotation axis, are highly disordered, with an occupancy of 0.5 for the different components. Due to the disorder and the quite low crystal quality, many restraints on bond lengths and displacement parameters had to be applied.

Crystal data and structure refinement parameters are given in Table 1 while selected bond lengths and angles are given in Table 2. The molecular plots were drawn using ORTEP-3,<sup>14</sup>

while the views of the packings were drawn using VESTA.<sup>15</sup> The topological analyses were done using TOPOS.<sup>16</sup>

### Luminescence measurements

Emission spectra were recorded on solid samples using a HORIBA Jobin Yvon Fluorolog spectrofluorimeter. The powdered complex was pressed between two silica plates that were mounted such that the faces were oriented vertically and at 45° to the incident excitation radiation. An excitation wavelength of 350 nm was used in all cases and the emission was monitored between 400 and 800 nm, with a 400 nm bandpass filter to block transmission of the excitation radiation.

## Results and discussion

### Synthesis

Extensive variations in the composition of reaction mixtures were made during the search for conditions providing insoluble crystalline products and only those which were successful (in the sense that a crystal structure was ultimately resolved) are reported in the Experimental section herein. The composition of the isolated materials revealed (see next section) that not only was the nature of the solvent mixture important but that the nature of any added cations and the quantity of any added base could also play a role. Thus, in acetonitrile–water solvent, the use of LiOH in a quantity beyond that required to simply neutralise the camphoric acid present provided, unsurprisingly, an oligomeric product containing hydroxide as a ligand but one in which Li<sup>+</sup> was not present.

In contrast, the use of just enough KOH to neutralise the acid gave a product without hydroxo-ligands but in the form of a K<sup>+</sup> complex. Neither 1 nor 2 contained the acid and uranyl moieties in the ratio in which they were originally mixed, illustrating the difficulties involved in developing rational synthetic procedures in these labile systems. Given the conditions of the syntheses under which even basic information such as the acidity constants for the organic acid and the metal aqua-ions is lacking, it is clear that much remains to be learned about these reactions. In the absence of an added base and with NMP–water as solvent, it is interesting that not only was any oligomerisation *via* hydroxo-bridging avoided but that also the camphorate was bound in the isolated crystals in its fully deprotonated form (a common observation in solvothermal reactions). This may in part be a reflection of solubility factors but is presumably also influenced by the enhanced dissociation of the organic acid at high temperatures.

### Crystal structures

Two complexes were grown at 140 °C from water–acetonitrile, either in the presence of an excess of LiOH beyond that required to neutralise the acid or sufficient KOH to just neutralise it, with very different outcomes. Complex [(UO<sub>2</sub>)<sub>4</sub>(L)<sub>3</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O (1), obtained with LiOH, is devoid of Li<sup>+</sup> cations, but the excess OH<sup>−</sup> is in part present as a ligand, as in species where it seemingly arises as a result of aqua-ligand dissociation (“hydrolysis”) at the elevated temperatures of the syntheses.<sup>9,17</sup> The asymmetric unit contains twice the formula unit, with two nearly identical groups of four

**Table 1** Crystal data and structure refinement details

	1	2	3	4
Chemical formula	C <sub>30</sub> H <sub>58</sub> O <sub>29</sub> U <sub>4</sub>	C <sub>120</sub> H <sub>194</sub> K <sub>8</sub> O <sub>77</sub> U <sub>8</sub>	C <sub>15</sub> H <sub>23</sub> NO <sub>7</sub> U	C <sub>40</sub> H <sub>60</sub> CuN <sub>2</sub> O <sub>18</sub> U <sub>2</sub>
<i>M</i> /g mol <sup>−1</sup>	1834.88	5085.79	567.37	1396.50
Crystal system	Monoclinic	Trigonal	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>R</i> 3	<i>P</i> 2 <sub>1</sub>	<i>C</i> 2
<i>a</i> /Å	15.4579(16)	21.3657(7)	9.2051(2)	19.5109(15)
<i>b</i> /Å	19.1439(17)	21.3657(7)	19.3999(3)	18.8200(10)
<i>c</i> /Å	17.1090(10)	38.4108(14)	10.3663(2)	13.9091(11)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	105.241(6)	90	97.9411(7)	109.813(4)
<i>γ</i> /°	90	120	90	90
<i>V</i> /Å <sup>3</sup>	4884.9(7)	15 185.1(13)	1833.44(6)	4805.0(6)
<i>Z</i>	4	3	4	4
<i>D</i> <sub>calcd</sub> /g cm <sup>−3</sup>	2.495	1.668	2.055	1.930
<i>μ</i> (Mo Kα)/mm <sup>−1</sup>	13.308	6.614	8.887	7.234
<i>F</i> (000)	3352	7254	1072	2684
Reflections collected	147 323	137 837	116 055	79 699
Independent reflections	18 496	12 834	11 154	12 387
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	12 679	8979	10 445	8355
<i>R</i> <sub>int</sub>	0.055	0.092	0.023	0.034
Parameters refined	1150	664	478	609
<i>R</i> <sub>1</sub>	0.071	0.063	0.038	0.068
<i>wR</i> <sub>2</sub>	0.186	0.169	0.101	0.194
<i>S</i>	1.016	1.055	1.079	1.042
Δρ <sub>min</sub> /e Å <sup>−3</sup>	−2.21	−1.53	−1.66	−1.83
Δρ <sub>max</sub> /e Å <sup>−3</sup>	2.67	2.21	2.49	1.58
Flack parameter	0.137(17)	0.070(13)	0.023(8)	0.117(16)

**Table 2** Environment of the metal atoms in compounds 1–4: selected bond lengths (Å) and angles (°)<sup>a</sup>

<b>1<sup>b</sup></b>	U1–O1	1.80(2)	O1–U1–O2	176.0(8)	<b>2</b>	U1–O1	1.794(10)	O1–U1–O2	179.0(5)
	U1–O2	1.701(18)	O17–U1–O19	77.6(6)		U1–O2	1.787(11)	O9–U1–O10	52.2(3)
	U1–O17	2.291(13)	O19–U1–O31	81.7(6)		U1–O9	2.440(11)	O10–U1–O13	66.9(3)
	U1–O19	2.413(15)	O31–U1–O23	74.0(5)		U1–O10	2.430(11)	O13–U1–O14	52.7(3)
	U1–O23	2.501(17)	O23–U1–O24	51.3(5)		U1–O13	2.451(10)	O14–U1–O17	66.0(3)
	U1–O24	2.437(16)	O24–U1–O17	75.6(6)		U1–O14	2.505(10)	O17–U1–O18	52.5(4)
	U1–O31	2.414(16)				U1–O17	2.496(9)	O18–U1–O9	69.8(4)
	U2–O3	1.74(2)	O3–U2–O4	173.0(8)		U1–O18	2.484(11)		
	U2–O4	1.83(2)	O17–U2–O20	76.9(6)		U2–O3	1.761(12)	O3–U2–O4	177.9(5)
	U2–O17	2.334(14)	O20–U2–O32	81.4(6)		U2–O4	1.771(11)	O11–U2–O12	54.0(4)
	U2–O20	2.318(18)	O32–U2–O27	76.1(6)		U2–O11	2.464(11)	O12–U2–O19 <sup>i</sup>	67.2(4)
	U2–O27	2.496(17)	O27–U2–O28	51.9(5)		U2–O12	2.409(12)	O19 <sup>i</sup> –U2–O20 <sup>i</sup>	51.0(4)
	U2–O28	2.410(15)	O28–U2–O17	73.9(5)		U2–O19 <sup>i</sup>	2.425(11)	O20 <sup>i</sup> –U2–O21	67.6(4)
	U2–O32	2.348(14)				U2–O20 <sup>i</sup>	2.470(12)	O21–U2–O22	52.6(4)
	U3–O5	1.862(14)	O5–U3–O6	175.3(8)		U2–O21	2.466(11)	O22–U2–O11	67.7(4)
	U3–O6	1.82(2)	O18–U3–O21 <sup>i</sup>	76.0(7)		U2–O22	2.445(12)		
	U3–O18	2.262(13)	O21 <sup>i</sup> –U3–O33	82.1(7)		U3–O5	1.749(18)	O5–U3–O6	180
	U3–O21 <sup>i</sup>	2.343(19)	O33–U3–O29	76.8(6)		U3–O6	1.757(18)	O15–U3–O16	51.5(3)
	U3–O29	2.525(16)	O29–U3–O30	51.2(5)		U3–O15	2.449(10)	O16–U3–O15 <sup>i</sup>	68.5(3)
	U3–O30	2.440(18)	O30–U3–O18	74.3(6)		U3–O16	2.504(10)		
	U3–O33	2.456(18)				U4–O7	1.751(19)	O7–U4–O8	180
	U4–O7	1.82(2)	O7–U4–O8	179.4(9)		U4–O8	1.726(17)	O23–U4–O24	52.8(4)
	U4–O8	1.756(16)	O18–U4–O22 <sup>i</sup>	74.5(6)		U4–O23	2.527(11)	O24–U4–O23 <sup>i</sup>	67.3(4)
	U4–O18	2.254(13)	O22 <sup>i</sup> –U4–O34	83.7(7)	<b>4</b>	U4–O24	2.482(11)		
	U4–O22 <sup>i</sup>	2.40(2)	O34–U4–O25	74.8(7)		U1–O1	1.785(10)	O1–U1–O2	178.2(4)
	U4–O25	2.582(19)	O25–U4–O26	52.2(6)		U1–O2	1.753(10)	O5–U1–O6	54.4(3)
	U4–O26	2.508(16)	O26–U4–O18	74.8(6)		U1–O5	2.430(8)	O6–U1–O14	77.0(3)
	U4–O34	2.413(18)				U1–O6	2.445(9)	O14–U1–O9	76.9(3)
<b>3</b>	U1–O1	1.775(6)	O1–U1–O2	178.0(3)		U1–O9	2.321(9)	O9–U1–O17	78.6(4)
	U1–O2	1.756(6)	O5–U1–O9	76.8(2)		U1–O14	2.338(9)	O17–U1–O5	73.2(3)
	U1–O5	2.297(6)	O9–U1–O13	81.3(2)		U1–O17	2.386(7)		
	U1–O9	2.357(6)	O13–U1–O11 <sup>i</sup>	73.6(2)		U2–O3	1.785(10)	O3–U2–O4	178.7(5)
	U1–O11 <sup>i</sup>	2.490(6)	O11 <sup>i</sup> –U1–O12 <sup>i</sup>	52.81(19)		U2–O4	1.780(11)	O7 <sup>i</sup> –U2–O8 <sup>i</sup>	53.1(3)
	U1–O12 <sup>i</sup>	2.429(6)	O12 <sup>i</sup> –U1–O5	75.52(19)		U2–O7 <sup>i</sup>	2.444(9)	O8 <sup>i</sup> –U2–O18	76.3(4)
	U1–O13	2.343(6)				U2–O8 <sup>i</sup>	2.425(10)	O18–U2–O11 <sup>j</sup>	75.3(4)
	U2–O3	1.780(8)	O3–U2–O4	179.1(3)		U2–O11 <sup>j</sup>	2.342(11)	O11 <sup>j</sup> –U2–O15	79.0(4)
	U2–O4	1.755(7)	O6–U2–O10	84.9(2)		U2–O15	2.387(8)	O15–U2–O7 <sup>i</sup>	76.3(3)
	U2–O6	2.341(6)	O10–U2–O7 <sup>j</sup>	75.4(2)		U2–O18	2.406(7)		
	U2–O10	2.330(6)	O7 <sup>j</sup> –U2–O8 <sup>j</sup>	52.5(2)		Cu–O1	2.657(10)	O1–Cu–O3	176.9(4)
	U2–O7 <sup>j</sup>	2.460(6)	O8 <sup>j</sup> –U2–O14	71.2(2)		Cu–O3	2.517(10)	O10–Cu–O12 <sup>j</sup>	178.1(5)
	U2–O8 <sup>j</sup>	2.406(7)	O14–U2–O6	76.1(2)		Cu–O10	1.968(9)	O13–Cu–O16	178.2(5)
	U2–O14	2.363(6)				Cu–O12 <sup>j</sup>	1.941(10)		
						Cu–O13	1.918(8)		
						Cu–O16	1.942(9)		

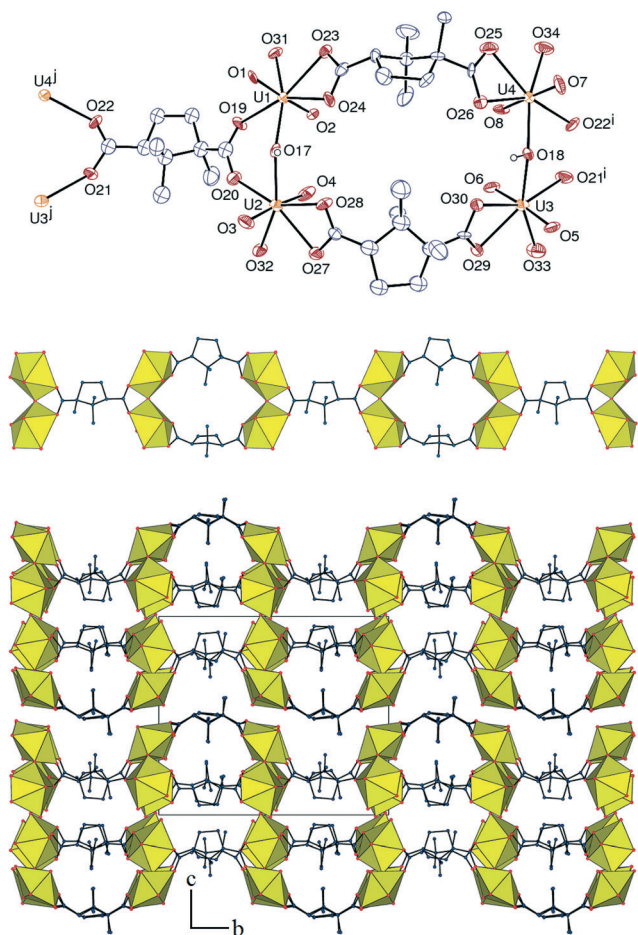
<sup>a</sup> Symmetry codes. 1:  $i = x, y + 1, z$ . 2:  $i = 1 - y, x - y, z$ . 3:  $i = -x, y - 1/2, 1 - z$ ;  $j = 1 - x, y + 1/2, 2 - z$ . 4:  $i = 3/2 - x, y - 1/2, 2 - z$ ;  $j = 3/2 - x, y + 1/2, 2 - z$ . <sup>b</sup> Values are given for only one of the two independent sets of four uranium atoms.

uranyl ions and three  $L^{2-}$  ligands. In each of these groups, the four cations are assembled into a macrocyclic subunit by two bis-chelating camphorate anions and two hydroxide ions, and the third  $L^{2-}$  ligand bridges two such rings in a bis(bridging bidentate) fashion (four monodentate oxygen atoms) (Fig. 1). Each uranyl ion is bound to one chelating carboxylate, one monodentate carboxylate, one hydroxide and one water ligand, with unexceptional average U–O bond lengths of 2.47(5), 2.36(3), 2.29(4) and 2.41(3) Å, respectively (the quite large standard uncertainties may be an effect of the rather low quality of the crystals and the structure refinement; see Experimental). The uranium coordination environment geometry is pentagonal bipyramidal. The large ring formed by the chelating  $L^{2-}$  ligands is flanked on two sides by smaller six-membered rings formed by the bridging

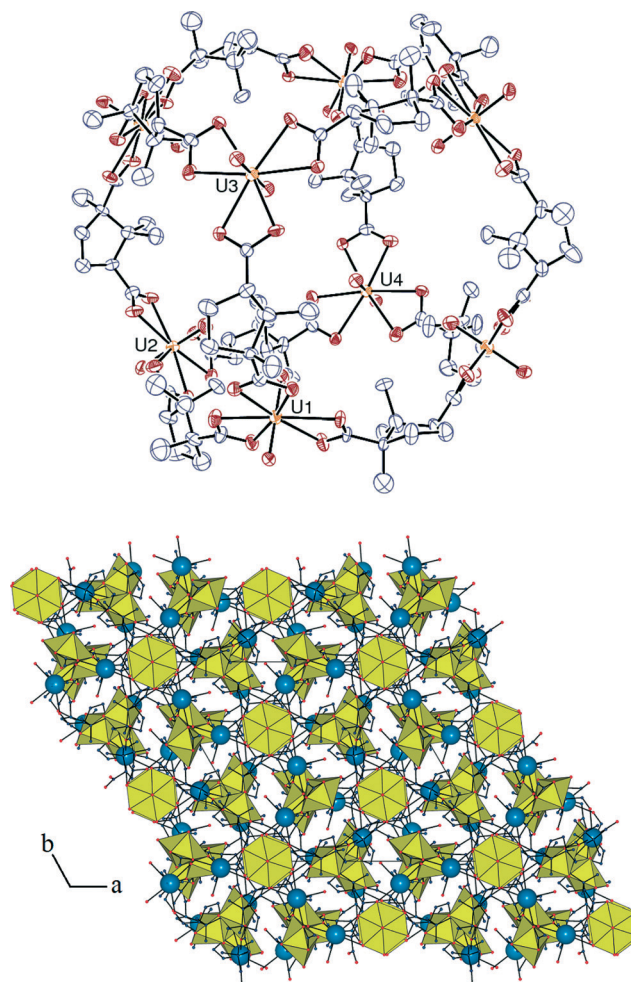
bidentate carboxylates and the hydroxide oxygen atoms. Each crystallographically independent connected group forms a one-dimensional coordination polymer directed along the  $b$  axis, with the total point (Schläfli) symbol  $\{4 \cdot 8^2\}_4 \{4^2\}_4 \{4\}_2 \{8\}_2$  (with symbols relative to the uranium atoms, bridging bidentate ligand, hydroxide ions, and chelating ligands, respectively). The two families of chains run side-by-side, with the uranium atoms, if considered alone, related by a non-crystallographic inversion centre suppressed by the presence of the  $L^{2-}$  ligands. The hydroxyl groups are hydrogen-bonded to lattice water molecules, and neighbouring chains are linked to one another by hydrogen bonds involving both complexed and free water molecules.

The compound obtained in the presence of  $K^+$ ,  $[(UO_2)_8K_8(L)_{12}(H_2O)_{12}] \cdot H_2O$  (2), is a heterometallic uranyl–potassium





**Fig. 1** Top: view of one of the two crystallographically independent units in complex 1. Solvent molecules and hydrogen atoms (except those of hydroxide ions) are omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes:  $i = x, y + 1, z$ ;  $j = x, y - 1, z$ . Middle: view of the 1D assembly. Bottom: view of the packing. Uranium coordination polyhedra are represented, and solvent molecules and hydrogen atoms are omitted in the last two views.



**Fig. 2** Top: view of complex 2. Displacement ellipsoids are drawn at the 30% probability level. Potassium atoms, water molecules and hydrogen atoms are omitted. Bottom: view of the packing down the trigonal axis. For clarity, only the two fully occupied potassium sites are represented. Solvent molecules and hydrogen atoms are omitted.

species with an overall structure close to that of the uranyl-barium complex  $[\text{Ba}(\text{H}_2\text{O})_8]_2[(\text{UO}_2)_8\text{Ba}_2(\text{L}_{12})(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ ,<sup>6b</sup> possibly reflecting the similar ionic radii of  $\text{Ba}^{2+}$  and  $\text{K}^+$ . The  $[(\text{UO}_2)_8(\text{L}_{12})]^{8-}$  octanuclear cage (Fig. 2) is similar to that in the former complex, and hence, it will not be described in detail. The only major difference is related to the symmetry of the assembly, since the barium-containing complex crystallizes in the tetragonal space group  $I4$ , with two uranium ions in the asymmetric unit, while 2 crystallizes in the trigonal space group  $R3$ , with four uranium atoms in the asymmetric unit, two of them ( $\text{U3}$  and  $\text{U4}$ ) located on a three-fold rotation axis. The potassium ions occupy four sites in general positions, two of them with partial occupancies (see Experimental), and they connect the cages through carboxylate bonding to form a three-dimensional framework. No crystalline material was obtained from water–acetonitrile when the reaction was performed with the addition of NaOH (one equivalent) instead of KOH, but this is perhaps only a reflection of the commonly observed large differences in the solubilities of analogous Na and K salts.

The complex  $[\text{UO}_2(\text{L})\text{MeOH}] \cdot \text{MeOH}$ , as previously reported,<sup>6a</sup> was, however, crystallized from 2:1 methanol–water in the presence of one equivalent NaOH and, as with complex 2, it does not contain hydroxo ligands.

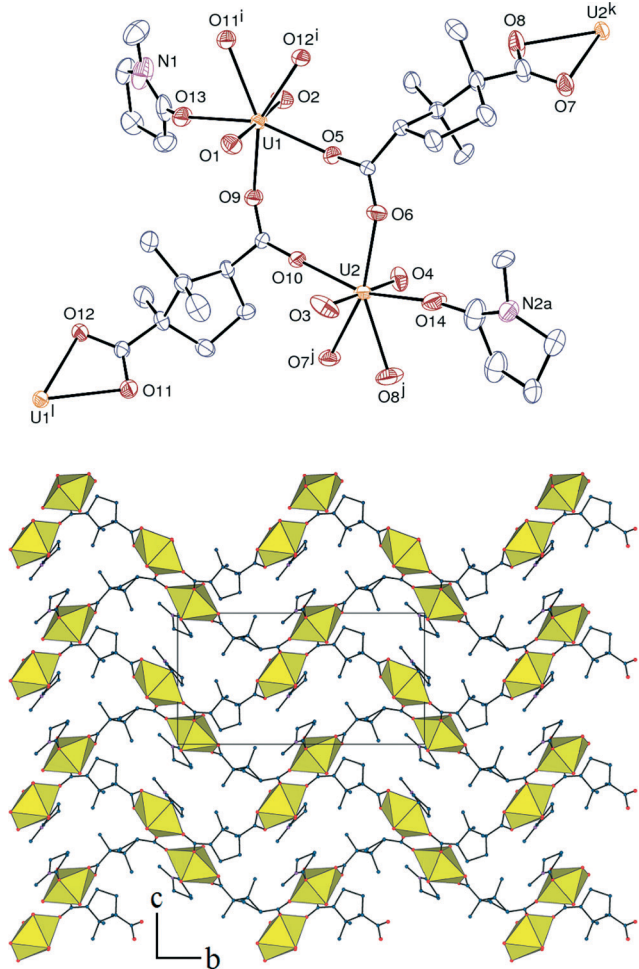
These syntheses with acetonitrile as co-solvent provided single crystals of moderate quality in low yield, which prompted us to find a more suitable solvent. Although NMP has only recently been used in solvo-/hydrothermal syntheses of uranyl–organic assemblies,<sup>7d,8b</sup> it is a thermally stable coordinating solvent better adapted than  $N,N$ -dimethylformamide, which is hydrolysed into formic acid and dimethylamine under heating. Previous results obtained with several polycarboxylic acids (Kemp's triacid, terephthalic, 2,5-thiophenedicarboxylic, 1,3,5-benzenetriacetic and nitrilotriacetic acids) have shown the potential of NMP for the synthesis of novel and sometimes unusual uranyl–organic species. NMP is most often present as a co-ligand in the final compounds, and it may thus have a strong influence on the architecture of the species formed (only one example of NMP coordination to the uranyl ion was

known before this work was undertaken,<sup>18</sup> but 20 structures containing other *N*-alkyl derivatives of 2-pyrrolidone, and the latter itself in one case, are reported in the CSD). Two complexes could be isolated from the reaction of uranyl nitrate with camphoric acid in water–NMP, one of them including additional Cu(II) cations.

The asymmetric unit in the complex [UO<sub>2</sub>(L)(NMP)] (3) contains twice the formula unit, with the two independent uranyl ions in similar environments (Fig. 3). Each of them is chelated by one carboxylate group and bound in a monodentate fashion to two adjacent oxygen atoms of bridging bidentate groups from two different L<sup>2−</sup> ligands and to one NMP molecule. The average U–O bond lengths of 2.45(3) and 2.33(2) Å for chelating and monodentate carboxylates, respectively, and of 2.353(10) Å for NMP, are unexceptional (the U–O bond length with NMP is 2.368(4) Å in the other complex reported<sup>18</sup>). While each cation is bound to three L<sup>2−</sup> ligands, each ligand is bound to three cations with different

bonding modes for its two carboxylate groups. Uranyl dimers with double carboxylate bridges are thus formed, which are connected to one another by the chelating groups, giving rise to a planar 2D assembly parallel to (1 0  $\bar{1}$ ), with the total point symbol {4·8<sup>2</sup>} (all nodes are equivalent). The sheets are stacked so as to form very narrow channels (~14 × 4 Å) along the *a* axis, in which the NMP molecules and some camphorate methyl groups are located. Such an arrangement displaying channels obstructed by NMP molecules has previously been encountered with other polycarboxylates.<sup>8b</sup> It may be indicative of structure-directing effects exerted by NMP molecules, with the drawback that no free space is present. The sheets in 3 are tightly stacked due to the absence of counter-ions or solvent molecules, with no significant inter-layer free space.

The complex [(UO<sub>2</sub>)<sub>2</sub>Cu(L)<sub>3</sub>(NMP)<sub>2</sub>] (4) was also obtained in water–NMP, with the additional presence of copper(II) nitrate. The latter, as a strong Lewis acid, was used so as to possibly increase the dimensionality of the species formed, as often observed in uranyl–organic assemblies.<sup>8b,9c,19</sup> The asymmetric unit in 4 corresponds to one formula unit, and the two crystallographically independent uranyl ions are in similar environments (Fig. 4). As in complex 3, each uranyl ion is bound to one chelating carboxylate group, two monodentate carboxylate oxygen atoms and one NMP molecule, with average U–O bond lengths of 2.436(9), 2.35(2) and 2.396(10) Å, respectively. The copper(II) cation is bound to four monodentate oxygen atoms from four different L<sup>2−</sup> ligands resulting in a square planar environment, and it makes two much longer axial contacts (>2.5 Å) with two uranyl oxo groups, thus giving one more example of a so-called cation–cation interaction involving a d-block metal cation.<sup>9a,19a,i,l,m,20</sup> The Cu–O(oxo) elongated axial bond lengths in 4 are comparable to those previously reported (2.41–2.59 Å),<sup>9a,19i,20a,b</sup> while the corresponding U–O(oxo) bond lengths do not display a significant lengthening. Two L<sup>2−</sup> ligands are complete and undisordered anions, while the third corresponds to two halves much disordered around twofold rotation axes (see Experimental). One of the former is bis-chelating while the other and the disordered halves are bis(bridging bidentate), connecting uranium and copper atoms through each of their carboxylate groups. A 2D assembly is thus generated, which is parallel to (0 0 1) and has the total point symbol {4·8<sup>2</sup>}<sub>2</sub>{4<sup>2</sup>·8<sup>3</sup>·10}{4<sup>2</sup>·8<sup>4</sup>}<sub>2</sub>{8} (if Cu–O(oxo) bonds are disregarded for simplicity), with successive symbols for uranium atoms, copper atoms, bridging bidentate and bis-chelating L<sup>2−</sup> ligands. It is notable that the cation–cation interactions do not bring a dimensionality increase by themselves in this case; however, the copper ions are necessary for the formation of the sheets by connecting ladder-shaped uranyl camphorate ribbons directed along the *b* axis. The layers formed are quite thick (~14 Å between the planes defined by the outermost carbon atoms of the protruding camphorate ligands), with the uranyl ions being located near the two surfaces and the copper ions inside. The packing is very compact and no significant free space is present.



**Fig. 3** Top: view of complex 3. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted and only one position of the disordered part is represented. Symmetry codes: *i* = −*x*, *y* − 1/2, 1 − *z*; *j* = 1 − *x*, *y* + 1/2, 2 − *z*; *k* = 1 − *x*, *y* − 1/2, 2 − *z*; *l* = −*x*, *y* + 1/2, 1 − *z*. Bottom: view of the 2D assembly with hydrogen atoms omitted.



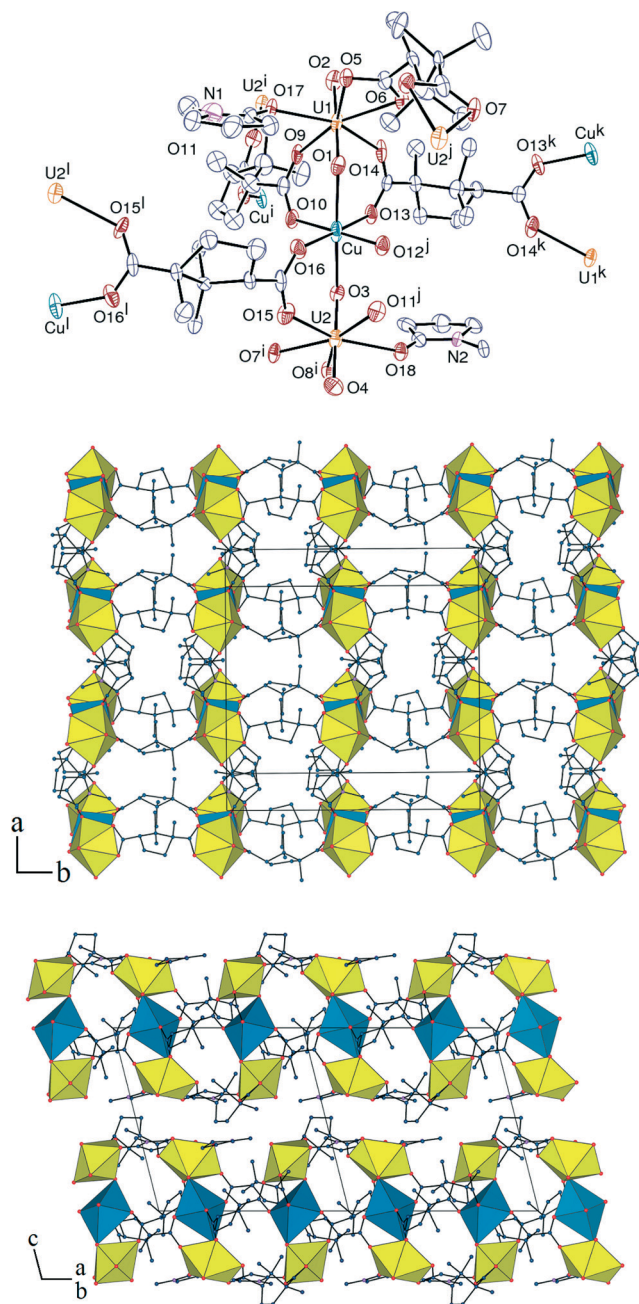


Fig. 4 Top: view of complex 4. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes:  $i = 3/2 - x, y - 1/2, 2 - z$ ;  $j = 3/2 - x, y + 1/2, 2 - z$ ;  $k = 2 - x, y, 2 - z$ ;  $l = 1 - x, y, 2 - z$ . Middle: view of the 2D assembly. Bottom: packing with the sheets viewed edge-on. Uranium coordination polyhedra are shown in yellow, while those of copper are shown in blue. Only one position of the disordered parts is represented and hydrogen atoms are omitted in all views.

### Luminescence properties

The emission spectra under direct uranyl excitation at a wavelength of 350 nm in the solid state were recorded for compounds 3 and 4, of which pure samples could be obtained (Fig. 5). Compound 3 displays the usual series of fine structure vibronic bands in the ~460–600 nm range<sup>21</sup> which correspond to the  $S_{11} \rightarrow S_{00}$  and  $S_{10} \rightarrow S_{0v}$  ( $v = 0-4$ ) electronic

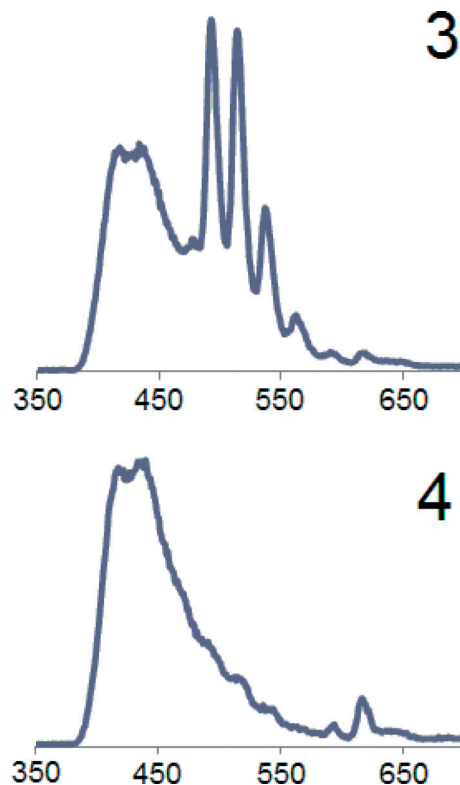


Fig. 5 Solid state luminescence spectra of complexes 3 and 4. Excitation wavelength: 350 nm; horizontal scale: wavelength (nm); vertical scale: emission intensity (arbitrary units).

transitions,<sup>22</sup> with the main maxima at 492 (s), 513 (s), 536 (m) and 561 (w) nm, a usual pattern in uranyl complexes.<sup>23</sup> The vibronic splitting energy of the  $S_{10} \rightarrow S_{0v}$  transitions is  $\sim 833 \text{ cm}^{-1}$ , smaller than the value of  $852 \text{ cm}^{-1}$  in uranyl malonates.<sup>22</sup> In addition, the spectrum displays a very broad band with a maximum at 410–440 nm which is attributable to the camphorate anion since it is observed in the spectrum of sodium camphorate (but not in that of camphoric acid, which is nearly featureless). It would appear that any energy transfer from the camphorate to uranyl is inefficient so that emission from both centres is observed. The spectrum of compound 4 shows only the latter broad band, and two weak bands at  $\sim 593$  and  $616 \text{ nm}$ . Uranyl luminescence appears to be quenched by copper(II) ions, as previously observed,<sup>8b,19h,24</sup> due to energy transfer to the d–d absorption band and non-radiative decay. Crystals of compounds 1–3 are pale yellow, showing that green luminescence is weak, while crystals of 4 are light green, as expected from the combined absorption of uranyl and copper(II) ions.

### Conclusions

Four uranyl complexes with the enantiopure (1*R*,3*S*)-(+)-camphorate ligand were synthesized under solvo-/hydrothermal conditions, with either acetonitrile or NMP as the organic component. In all cases, the complexes crystallize in chiral space groups and are enantiopure, but their geometry is strongly dependent on the experimental conditions used. Complexes 1 and 2 were

obtained in water–acetonitrile under basic and neutral conditions, respectively. Whereas the former is a 1D coordination polymer, the second is an octanuclear uranyl camphorate cage analogous to those obtained in the presence of DABCO under purely hydrothermal conditions, with the molecular subunits being assembled into a 3D framework by potassium cations. A quite similar assembly was previously obtained with barium(II) cations, which suggests that its formation is favoured by larger alkali or alkaline-earth cations. However, the more basic medium in the case of LiOH may also play a role in favouring hydrolysis and crystallization of a hydroxide-containing species. The two complexes obtained in water–NMP, **3** and **4**, are characterized by the complete absence of hydrolysis products, as previously noticed,<sup>7d,8b</sup> and also of water (the latter is not always true since uranyl complexes with Kemp's triacid crystallized under similar conditions contain both coordinated and free water molecules<sup>7d</sup>). In addition to the use of low-pH solutions<sup>25</sup> or high-halide media,<sup>9d,26</sup> solvo-/hydrothermal conditions with NMP as the organic component thus appear to be an effective way to avoid the formation of highly unpredictable hydrolysis products. NMP is particularly suitable for that since it resists hydrolysis and thus does not induce pH changes. Further, NMP is coordinated in both complexes **3** and **4** and has, consequently, a strong effect on the final architecture. In contrast to some of the polycarboxylates previously investigated in the presence of NMP (terephthalate, 2,5-thiophenedicarboxylate, and nitrilotriacetate)<sup>8b</sup> from which 3D frameworks were generated, 2D assemblies only are formed with camphorate, one of them displaying a central unit occupied by copper(II) ions surrounded by two uranyl-containing outer layers. In these as well as in previous uranyl complexes, the camphorate ligand, always dianionic, is bound through its four oxygen atoms and has only three coordination modes (bis(chelating), bis(bridging bidentate) and chelating/bridging bidentate), except in compound **2** in which chelation is associated to additional bonding to potassium cations. It thus appears as a dicarboxylate ligand which behaves in a quite consistent way. Finally, while complex **3** displays the usual uranyl luminescence fine structure in the emission spectrum, having the band positions as expected for the pentagonal bipyramidal geometry about the uranium atom, quenching due to copper(II) ions occurs in **4**.

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